This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problems Mailbox.

(19) Europäisch s Pat ntamt
Europ an Patent Office
Office europé n des br vets

(11) Publication number: **0 459 472 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **02.08.95** (51) Int. Cl.[6]: **C08K 9/04**, C08L 79/00

(21) Application number: **91108838.3**

(22) Date of filing: **29.05.91**

(54) Polyimide composite material and process for producing the same.

(30) Priority: **30.05.90 JP 140372/90**

(43) Date of publication of application:
04.12.91 Bulletin 91/49

(45) Publication of the grant of the patent:
02.08.95 Bulletin 95/31

(84) Designated Contracting States:
DE GB

(56) References cited:
DE-A- 3 803 075
DE-A- 3 806 548
DE-A- 3 810 006
US-A- 4 775 686

(73) Proprietor: **KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO**
41-1, Aza Yokomichi
Oaza Nagakute
Nagakute-cho
Aichi-gun
Aichi-ken, 480-11 (JP)

(72) Inventor: **Yano, Kazuhisa**
Narumi-shataku 336,
84-1 Aza Otokoyama,
Narumi-cho
Midori-ku,
Nagoya-shi,
Aichi-ken, 458 (JP)
Inventor: **Usuki, Arimitsu**
A-304, 2, Kinjo 1-chome,
Kita-ku
Nagoya-shi,
Aichi-ken, 462 (JP)
Inventor: **Okada, Akane**
2-333, Momoyama-cho
Obu-shi,
Aichi-ken, 474 (JP)
Inventor: **Kurauchi, Toshio**
Shimadabashi-jutaku 2-407, 2-301, Shimada
Tempaku-ku,
Nagoya-shi,
Aichi-ken, 468 (JP)

(74) Representative: **Blumbach, Kramer & Partner**
Patentanwälte
Radeckestrasse 43
D-81245 München (DE)

Not : Within nin months from the publication of the mention of the grant of th European patent, any person may give notice to the European Pat nt Office of opposition to the European patent granted. Notic of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 459 472 B1

Descripti n

The present invention relates to a polyimide composite material and a process for producing the same, and more particularly, it is concerned with a polyimide composite material which is compos d of a polyimide-containing resin (hereinafter referred to as a polyimide resin) and a layered clay mineral dispersed therein and has improved water and gas barrier properties, and also with a process for producing the same.

Polyimide is suitable for use as film, flexible printed circuit board, motor insulator, wire covering, etc. on account of its outstanding thermal properties, mechanical properties, electrical insulating properties, and chemical resistance. However, it poses a problem associated with practical use because of its poor gas (and water vapor) barrier properties and high coefficient of thermal expansion.

This problem has been addressed by introducing a fluorinated monomer into the molecule (as disclosed in JP-A 60933/1990 and JP-A 60934/1990) or by incorporating an inorganic substance (as such) into polyimide. To address a similar problem involved in polyamide resins, there has been proposed a composite material composed of a polyamide resin and a layered clay mineral dispersed therein which has previously been intercalated with an organic compound (US-A 4,739,007)

The approach to solution by the aid of fluorinated monomer is not of practical value because of its high price. The mere incorporation of an inorganic substance (as such) into a polyimide resin ends up with incomplete dispersion due to their poor affinity, without achieving the improvement in gas barrier properties as intended, and a film formed of such composite material will lack the surface smoothness.

The technology of the polyamide composite material mentioned above cannot be applied to polyimide because of their difference in affinity for solvents. In other words, polyimide is produced by polymerization in a special solvent (i.e., aprotic polar solvent), and a clay mineral intercalated with organic compound usually has a weak affinity for such a special solvent. For this reason, a clay mineral does not disperse well in a polyimide.

There are disclosed in US-A 4,775,586 composites and construction materials which are composed of a polyimide and a flocculant of intercalated clay formed by the reaction of a layered clay mineral with organic dionium ions. This patented invention is intended for flocculation rather than dispersion of intercalated clay into a polyimide resin. Therefore, this polyimide composite material does not have good gas and water barrier properties.

DE-A 38 10 006 discloses a process for the manufacture of a composite material comprising a polymer and a layered silicate clay material wherein the silicate material is bound to the polymer via ionic bonds. The silicate clay material is swollen by an onium group-containing material wherein the onium compound contains a further functional group which is capable of binding to the polymer. Although it is stated in the Abstract of said document that the layered silicate is uniformly dispersed in the composite material, there is no indication or example, respectively showing the uniform dispersion of the layered silicate material in the polymer.

DE-A 38 06 548 also discloses a composite material and a process for its manufacture. In particular, comparative example 3 on page 10 of said document indicates that a polymethyl methacrylate polymer containing a clay mineral intercalated with a mono-onium compound has inferior strength properties when the mono-onium compound has no functional group at the terminal end of the carbon chain, compared to the case where the mono-onium compound has a further functional group. However, anything with respect to the improvement of the gas barrier properties could not be learnt from said prior art document. However, an improvement of the gas and water barrier properties was intended in accordance with the present invention.

The gist of the present invention resides in a polyimide composite material which comprises a polyimide-containing resin (referred to as a polyimide resin) and a layered clay mineral intercalated with organic onium ions and dispersed in the polyimide as claimed. A layered clay mineral intercalated with organic onium ions has an affinity for the polyimide. The gist of the present invention resides also in a process for producing a polyimide composite material which comprises the steps of intercalating a layered clay mineral with organic onium ions, adding by mixing the intercalated product to a solution of a monomer or prepolymer for polyimide, removing the solvent, and forming a polyimide as claimed.

Oth r and further obj cts, featur s, and advantages of th pr s nt inv ntion will app ar mor fully from the following description.

The present invention concerns a polyimide composite material which comprises 0.01 to 50 parts by weight of an intercalated clay mineral uniformly dispers d in 50 to 99.99 parts by weight of a polyimid - containing resin, wherein said intercalated clay mineral is obtainable by reacting a layered clay mineral with organic mono-onium compounds having only one onium ion at one terminal of their main chain and being

free of amino, carboxyl, poxide, hydroxyl, vinyl and other functional groups capable of reacting with a polymer.

The present invention furthermore concerns a process for producing a polyimide composite material which comprises the st ps of

- intercalating a layered clay mineral with organic mono-onium compounds having only one onium ion at one terminal of their main chain and being free of amino, carboxyl, epoxide, hydroxyl, vinyl and other functional groups capable of reacting with a polymer by mixing in a protic polar solvent;
- adding, by mixing, the intercalated clay mineral from which said protic polar solvent is removed, to a solution obtained by dissolving a monomer or prepolymer for polyimide in an aprotic polar solvent;
- removing the aprotic polar solvent; and
- forming a polyimide composite material, wherein 0.01 to 50 parts by weight of said intercalated clay mineral is uniformly dispersed in 50 to 99.99 parts by weight of said polyimide.

The present invention is also embodied in a polyimide composite material which comprises a polyimide resin and a layered clay mineral dispersed therein which is intercalated with organic mono-onium ions according to claims 2 to 6 and a process for preparing them according to claims 8 to 10.

The polyimide composite material has good gas and water vapor barrier properties because it contains the layered clay mineral dispersed therein which physically prevents the diffusion of oxygen and water in the composite material. Therefore, it is suitable for use as a raw material for electrical insulation and printed circuit boards. It protects metal parts from oxidation and electrolytic corrosion by permeating oxygen and water vapor.

The polyimide composite material retains the polyimide's inherent properties-heat stability, mechanical strength, and chemical resistance, despite the layered clay mineral it contains. As a whole, it is superior to a polyimide resin used alone.

The polyimide composite material gives rise to a molded product having a good dimensional stability owing to the layered clay mineral which represses thermal expansion. It also gives rise to a film having a smooth surface owing to the layered clay mineral which is uniformly dispersed.

A polyimide-containing resin referred to as "polyimide resin" in the present invention includes all polyimide resins known and blends of a polyimide resin with other resins.

"Organic mono-onium ions" as used in the present invention denotes organic compounds having an onium ion at one terminal of the main chain. Examples of the mono-onium ion include monoammonium ion, monopyridinium ion, mono-phosphonium ion, and monosulfonium ion. The main chain may be a straight or branched carbon chain; it may have a ring structure in part thereof. The other terminal of the main chain has a hydrogen atom. The main chain should preferably have 6 or more carbon atoms so that the organic onium ion expands the interlayer distance of the clay to such an extent that the layered clay mineral is sufficiently dispersed. However, the main chain should preferably have less than 20 carbon atoms so that the organic mono-onium ion has a good affinity for protic polar solvents (e.g., water) and aprotic polar solvents. Preferred examples of the organic mono-onium ion are alkylammonium ions such as laurylamine ion, myristylamine ion, palmitylamine ion, and stearylamine ion.

"Layered clay mineral" as used in the present invention includes smectite clay minerals (such as montmorillonite, saponite, beidellite, hectorite, and stevensite), vermiculite, halloysite, and swellable mica. (Swellable mica collected by decantation is readily dispersible in water, and it lends itself to a good polyimide composite material even at as low a content as 0.01 wt%.) The layered clay mineral should preferably have a cation exchange capacity (CEC) of 50 to 300 meq/100 g and also have a large contact area for the polyimide or monomer to which it is added. With a CEC greater than 300 meq/100 g, the layered clay mineral has such a strong layer bond strength that it presents difficulties in the expansion of the layer distance and hence it does not disperse well in the polyimide. With a CEC smaller than 50 meq/100 g, the layered clay mineral absorbs the organic mono-onium ion only insufficiently and hence lacks affinity for the polyimide. It is desirable that the layered clay mineral be crushed to a desired shape before use by means of a mixer, mill, mortar, and the like, to facilitate its complete dispersion.

The intercalation of a layered clay mineral with organic mono-onium ions is based on the replacement of exchangeable inorganic ions in the layered clay mineral by the organic mono-onium ions. The ratio (by weight) of the organic mono-onium ions to the layered clay mineral is not specifically restricted; however, th amount of th organic mono-onium ions should b larg enough for th compl t r plac ment of th exchangeable inorganic ions.

The composite material of the pr sent inv ntion is composed of 50 to 99.99 parts by weight of polyimide and 0.01 to 50 parts by weight of layered clay mineral containing organic mono-onium ions. If the amount of polyimide is less than 50 parts by weight and th amount of intercalated clay mineral is more than 50 parts by weight, the resulting composite material is poor in mechanical properties and surface

smoothness. If the amount of intercalated clay mineral is less than 0.01 part by weight, the resulting composite material does not hav improved prop rties.

"Dispersion" of layered clay mineral in polyimide is defined as a state of dispersion in which the layered clay mineral is divided into individual unit layers at the molecular level. To be mor specific, th state of dispersion is such that more than 50%, preferably more than 70%, of the layered clay mineral is dispersed without forming a mass, with individual layers or groups of less than 5 layers (on average) orienting parallel to one another or randomly or both. When the composite material is formed into a film, the layered clay mineral is oriented in the direction parallel to the film surface, which contributes to barrier properties.

The composite material of the present invention may further include one or more optional resins such as polyetherether ketone, polysulfone, and polyamideimide for the control of desired physical properties. It may be further incorporated with pigments and dyes, reinforcements and fillers (such as glass fiber, metal fiber, metal flake, and carbon fiber), heat stabilizers, antioxidants, UV light absorbers, light stabilizers, lubricants, plasticizers, antistatic agents, and flame retardants according to the intended use.

The present invention is also embodied in a process for producing a polyimide composite material which comprises the steps of reacting a layered clay mineral with organic mono-onium compounds having only one onium group at one terminal of their main chain and being free of amino, carboxyl, epoxide, hydroxyl, vinyl and other functional groups capable of reacting with said polymer, thereby giving an intercalated clay mineral, adding by mixing the intercalated clay mineral to a solution of a monomer or prepolymer for polyimide, removing the solvent from the solution, and forming a polyimide.

The process of the present invention starts with intercalation of a layered clay mineral with organic mono-onium compounds having only one onium group at one terminal of their main chain and being free of amino, carboxyl, epoxide, hydroxyl, vinyl and other functional groups capable of reacting with said polymer. The intercalation expands the layer distance of the layered clay mineral, thereby enabling the layered clay mineral to take polymer molecules into the space between layers. Moreover, the layered clay mineral is given by the organic mono-onium ions an affinity for a solution of a monomer or prepolymer for polyimide. As the result, the intercalated clay mineral is mixed well with a monomer or prepolymer for polyimide. After the completion of polymerisation, there is obtained a polyimide composite material in which the layered clay mineral is thoroughly dispersed.

The same definitions as given earlier are also applied to those terms "layered clay mineral", "organic mono-onium ions", and "intercalated clay mineral" which are used to explain the process of the present invention.

No restrictions are placed on the process of preparing a layered clay mineral containing organic mono-onium ions. A typical process consists of mixing a layered clay mineral with organic mono-onium ions in a neat or mixed solvent selected from water, methanol, ethanol, propanol, isopropanol, ethylene glycol, 1,4-butanediol, and glycerin. A preferred solvent for montmorillonite is water, methanol, or ethanol, or a mixture of two or more of them.

According to the present invention, the process should employ a protic polar solvent such as water and alcohol. It is only this solvent which permits the good dispersion of layered clay mineral. This solvent is also a good one for the organic mono-onium ion.

The organic mono-onium ion used in the present invention should preferably be an alkyl onium ion which has less than 20 carbon atoms in the main chain. However, for the sufficient expansion of the layer distance of the layered clay mineral, it is desirable that the main chain of the organic mono-onium ion have 6 or more carbon atoms.

The polyimide in the present invention is produced from any dianhydride and diamine which are known as monomers for polyimide. Examples of the dianhydride include pyromellitic dianhydride, 3,3', 4,4'-biphenyltetracarboxylic dianhydride, and 3,3', 4,4-benzophenonetetracarboxylic dianhydride. Examples of the diamine include 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, and *p*-phenylenediamine. They may be used alone for homopolymerization or in combination with one another for copolymerization. They may be copolymerized with a dicarboxylic acid and a diol or their respective derivatives to give polyamideimide, polyesteramideimide, or polyesterimide.

The polyimide in the present invention is also produced from a prepolymer which is exemplified by poly(amic acid). Usually, a polyimide r sin cannot be mixed in its molten stat with the int rcalated clay mineral because it decomposes at a temperature lower than the temperature at which it b gins to flow. But, if the temperature of fluidization is lower than that of decomposition, the polyimide composite material can be produced by this melt-mixing method.

The dispersion of the intercalated clay mineral is effected by the aid of an aprotic polar solvent which is commonly used for the production of polyimide. Examples of this solvent include N,N-dimethylacetamide,

N-methylpyrrolidone, N,N-dim thylformamide, and 1,3-dim thylimidazolidinone and the like. They are only solvents which dissolve the monomer and prepolymer for polyimide. These solvents ar miscible also with the organic mono-onium ion and hence with th intercalated clay min ral. Therefore, th se solvents permit intimate mixing (at the molecular level) of the monomer or prepolymer for polyimid with the intercalated clay mineral.

EXAMPLES

The invention will now be explained with reference to the following examples. The polyimide composite material was evaluated by measuring water vapor permeability, oxygen permeability, and thermal expansion coefficient according to ASTM. The film prepared from the polyimide composite material was rated as good or poor according to the visual inspection of the external appearance.

Preparation of solution (A-1)

A solution of poly(amic acid) was prepared by completely dissolving 52.4 g of 4,4'-diaminodiphenyl ether in 516 g of dimethylacetamide and then adding to the solution 57.0 g of pyromellitic dianhydride.

Preparation of solution (A-2)

A solution of poly(amic acid) was prepared by completely dissolving 28.3 g of *p*-phenylenediamine in 700 g of dimethylacetamide and then adding to the solution 76.9 g of biphenyltetracarboxylic dianhydride.

Preparation of organophilic clay (B-2)

In 3 liters of water was dispersed 100 g of montmorillonite (from Yamagata Prefecture) having a cation-exchange capacity of 119 meq/100 g. To the dispersion was added 44.1 g of laurylamine and 24.1 g of conc. hydrochloric acid (36%), followed by stirring at room temperature for 60 minutes. After thorough rinsing, the intercalated montmorillonite including water was separated by filtration under reduced pressure using a Buchner funnel. The intercalated montmorillonite including water was freeze-dried to remove the water. Thus, intercalated montmorillonite containing ammonium ion of laurylamine was given. Finally, it was dispersed in 4.5 kg of dimethylacetamide.

Preparation of organophilic clay (B-3)

In 3 liters of water was dispersed 100 g of swellable mica having a cation-exchange capacity of 234 meq/100 g. To the dispersion was added 88.2 g of laurylamine and 48.2 g of conc. hydrochloric acid (36%), followed by stirring at room temperature for 60 minutes. After thorough rinsing, the intercalated mica including water was separated by filtration under reduced pressure using a Buchner funnel. The intercalated mica including water was freeze-dried to remove the water. Thus, intercalated swellable mica containing ammonium ion of laurylamine was given. Finally, it was dispersed in 4.5 kg of dimethylacetamide.

Preparation of organophilic clay (B-4)

In 3 liters of water was dispersed 100 g of synthetic saponite having a cation-exchange capacity of 119 meq/100 g. To the dispersion was added 44.1 g of laurylamine and 24.1 g of conc. hydrochloric acid (36%), followed by stirring at room temperature for 60 minutes. After thorough rinsing, the intercalated saponite including water was separated by filtration under reduced pressure using a Buchner funnel. The intercalated saponite including water was freeze-dried to remove the water. Thus, intercalated synthetic saponite containing ammonium ion of laurylamine was given. Finally, it was dispersed in 4.5 kg of dimethylacetamide.

Preparation of organophilic clay (B-5)

In 90 liters of water was dispersed 1.5 kg of swellable mica ("DM Clean A", made by Topy Kogyo Co., Ltd.), followed by standing for 24 hours. The cloudy supernatant liquid was collected. Thus there was obtained 100 g of swellable mica which is easily dispersible. It was dispers d in 3 liters of water. To the dispersion was added 88.2 g of laurylamine and 48.2 g of conc. hydrochloric acid (36%), followed by

stirring at room temperature for 60 minutes. After thorough rinsing, the intercalated mica including water was separated by filtration under reduced pressure using a Buchner funnel. The intercalated mica including water was freeze-dried to remove the water. Thus, intercalated swellable mica containing ammonium ion of laurylamine was giv n. Finally, it was disp rsed in 4.5 kg of dimethylac tamide.

Examples 2 to 7 and 9 to 13

Either of A-1 and A-2 (solution) prepared as mentioned above was combined with any one of B-2 to B-5 (dispersion) prepared as mentioned above according to the formulation shown in Table 1. The resulting mixture was made into film by casting, followed by heating at 300 °C for 2 hours. Thus there was obtained a polyimide film containing a clay mineral.

Comparative Examples 1 and 2

Either of A-1 and A-2 (poly(amic acid) solution) prepared as mentioned above was made into a film by casting, followed by heating at 300 °C for 2 hours. Thus there was obtained a polyimide film.

Comparative Example 3

A-1 (poly(amic acid) solution) prepared as mentioned above was incorporated with 2% montmorillonite (without intercalation). The resulting mixture was made into film by casting, followed by heating at 300 °C for 2 hours. Thus there was obtained a polyimide film containing plain montmorillonite.

Evaluation of polyimide films

The polyimide films obtained in Examples 2 to 7 and 9 to 13 and Comparative Examples 1 to 3 were tested for content (wt%) of layered clay mineral, water vapor permeability ($g \cdot mm/m^2 \cdot 24$ h), oxygen permeability ($cc \cdot mm/m^2 \cdot 24\ h \cdot atm$), and thermal expansion coefficient ($cm/cm \cdot °C$). The results are shown in Table 1.

It is noted from Table 1 that those films which contain a layered clay mineral have greatly improved gas barrier properties as indicated by low water vapor permeability and oxygen permeability, and also have a low thermal expansion coefficient and a good external appearance. By contrast, those films which are not incorporated with a layered clay mineral are poor in gas barrier properties and have a high thermal expansion coefficient. The film which is incorporated with a plain clay mineral (without intercalation) is poor in external appearance, gas barrier properties, and thermal expansion coefficient.

Table 1

Example No.	Combination	Mixing ratio A : B	Content of clay mineral	Water vapor permeability	Oxygen permeability	Thermal expansion coefficient	Film appearance
2	A-1 + B-2	99.3 : 0.7	0.1	2.1	9.5	2.9×10^{-5}	good
3	A-1 + B-2	81.8 : 18.2	3	0.82	3.5	2.6×10^{-5}	good
4	A-1 + B-2	61.5 : 38.5	8	0.25	1.2	2.2×10^{-5}	good
5	A-1 + B-2	38.8 : 61.2	18	0.03	0.2	1.5×10^{-5}	good
6	A-1 + B-3	72.5 : 27.5	5	0.51	2.1	2.4×10^{-5}	good
7	A-1 + B-4	81.8 : 18.2	3	0.77	3.3	2.6×10^{-5}	good
9	A-2 + B-2	77.9 : 22.1	5	0.41	1.6	1.6×10^{-5}	good
10	A-2 + B-4	68.1 : 31.9	8	0.19	0.8	1.5×10^{-5}	good
11	A-1 + B-5	99.86 : 0.14	0.02	2.1	9.3	2.8×10^{-5}	good
12	A-2 + B-5	98.6 : 1.4	0.2	1.2	4.8	2.1×10^{-5}	good
13	A-1 + B-5	81.8 : 18.2	3	0.1	0.8	0.8×10^{-5}	good
(1)	A-1	-	0	2.5	10.0	3×10^{-5}	good
(2)	A-2	-	0	2.0	8.2	2×10^{-5}	good
(3)	A-1	-	2	2.5	9.9	2.9×10^{-5}	poor
Comparative Examples are indicated by parenthesized numbers.							

Claims

1. A polyimide composite material which comprises 0.01 to 50 parts by weight of an intercalated clay mineral uniformly dispersed in 50 to 99.99 parts by weight of a polyimide-containing resin, wherein said intercalated clay mineral is obtainable by reacting a layered clay mineral with organic mono-onium compounds having only one onium ion at one terminal of their main chain and being free of amino, carboxyl, epoxide, hydroxyl, vinyl and other functional groups capable of reacting with a polymer.

2. A polyimide composite material as claimed in claim 1 wherein the organic mono-onium ion is at least one selected from the group consisting of monoammonium ion, monopyridinium ion, monophosphonium ion, and monosulfonium ion.

3. A polyimide composite material as claimed in claim 1 or claim 2 wherein the organic mono-onium ion has a main chain which is composed of 6 to 20 carbon atoms.

4. A polyimide composite material as claimed in any of claims 1 to 3 wherein th layered clay mineral is at least one selected from the group consisting of smectite clay minerals comprising montmorillonite, saponite, beidellite, hectorite, and stevensite; vermiculite; halloysite; and swellable mica.

5. A polyimide composite material as claimed in any of claims 1 to 4 wherein the intercalated layered clay mineral is dispersed such that individual layers are separated from one another at the molecular level.

6. A polyimide composite material as claimed in any of claims 1 to 5 which further contains at least one component selected from the group consisting of resins other than polyimide, pigments, dyes, glass fiber, metal fiber, metal flake, heat stabilizers, antioxidants, UV light absorbers, light stabilizers, lubricants, plasticizers, antistatic agents, and flame retardants.

7. A process for producing a polyimide composite material which comprises the steps of
   - intercalating a layered clay mineral with organic mono-onium compounds having only one onium ion at one terminal of their main chain and being free of amino, carboxyl, epoxide, hydroxyl, vinyl and other functional groups capable of reacting with a polymer by mixing in a protic polar solvent;
   - adding, by mixing, the intercalated clay mineral from which said protic polar solvent is removed, to a solution obtained by dissolving a monomer or prepolymer for polyimide in an aprotic polar solvent;
   - removing the aprotic polar solvent; and
   - forming a polyimide composite material, wherein 0.01 to 50 parts by weight of said intercalated clay mineral is uniformly dispersed in 50 to 99.99 parts by weight of said polyimide.

8. A process for producing a polyimide composite material as claimed in claim 7 wherein said protic polar solvent comprises at least one selected from the group consisting of water, methanol, ethanol, propanol, isopropanol, ethylene glykol, 1,4-butanediol, and glycerin.

9. A process for producing a polyimide composite material as claimed in claim 7 or claim 8 wherein said solution is a solution od poly(amic acid).

10. A process for producing a polyimide composite material as claimed in any of claims 7 to 9 wherein said aprotic polar solvent comprises at least one amide-type solvent selected from the group consisting of N,N-dimethylacetamide, N-methylpyrrolidone, N,N-dimethylformamide, and 1,3-dimethylimidazolidinone.

Patentansprüche

1. Polyimid-Verbundmaterial, welches 0,01 bis 50 Gew.-Teile eines Einlagerungen aufweisenden Tonminerals umfaßt, das einheitlich in 50 bis 99,99 Gew.-Teilen eines ein Polyimid enthaltenden Harzes dispergiert ist, wobei das Einlagerungen aufweisende Tonmineral erhältlich ist durch Umsetzen eines Schichten-Tonminerals mit organischen Mono-Onium-Verbindungen, die nur ein Onium-Ion an einem Ende ihrer Hauptkette aufweisen und frei sind von Amino-Gruppen, Carboxyl-Gruppen, Epoxid-Gruppen, Hydroxyl-Gruppen, Vinyl-Gruppen und anderen funktionellen Gruppen, die zur Umsetzung mit einem Polymer befähigt sind.

2. Polyimid-Verbundmaterial nach Anspruch 1, worin das organische Mono-Onium-Ion wenigstens eines ist, das gewählt ist aus der aus Monoammonium-Ion, Monopyridinium-Ion, Monophosphonium-Ion und Monosulfonium-Ion bestehenden Gruppe.

3. Polyimid-Verbundmaterial nach Anspruch 1 oder 2, worin das organische Mono-Onium-Ion eine Hauptkette aufweist, die aus 6 bis 20 Kohlenstoffatomen aufgebaut ist.

4. Polyimid-Verbundmaterial nach ein m der Ansprüch 1 bis 3, worin das Schicht n-Tonmin ral w nigstens eines ist, das gewählt ist aus der aus Smektit-Tonmineralien, die Montmorillonit, Saponit, Beid llit, Hectorit und Stevensit umfassen, V rmiculit, Halloysit und quellbarem Glimmer besteh nden Guppe.

5. Polyimid-Verbundmat rial nach einem der Ansprüch 1 bis 4, worin das Einlagerungen aufweisende Schichten-Tonmaterial in der Weise dispergiert ist, daß einzeln Schichten voneinander auf molekular m Niveau getrennt sind.

6. Polyimid-Verbundmaterial nach einem der Ansprüche 1 bis 5, welches weiter wenigstens eine Komponente enthalt, die gewählt ist aus der aus von Polyimid verschiedenen Harzen, Pigmenten, Farbstoffen, Glasfasern, Metallfasern, Metallflocken, Hitzestabilisatoren, Oxidationsinhibitoren, UV-Licht absorbierenden Mitteln, Lichtstabilisatoren, Gleitmittein, Weichmachern, Antistatik-Mitteln und flammhemmenden Mitteln bestehenden Gruppe.

7. Verfahren zur Herstellung eines Polyimid-Verbundmaterials, das die Schritte umfasst, daß man
   - ein Schichten-Tonmaterial mit Einlagerungen von organischen Mono-Onium-Verbindungen versieht, die nur ein Onium-Ion am Ende ihrer Hauptkette aufweisen und frei sind von Amino-Gruppen, Carboxyl-Gruppen, Epoxid-Gruppen, Hydroxyl-Gruppen, Vinyl-Gruppen und anderen funktionellen Gruppen, die zur Umsetzung mit einem Polymer befähigt sind, indem man dieses in ein protisches polares Lösungsmittel einmischt;
   - unter Mischen das mit Einlagerungen versehene Tonmineral, von dem das protische polare Lösungsmittel entfernt wird, einer Lösung zusetzt, die erhalten wird durch Lösen eines Monomers oder Prepolymers für ein Polyimid in einem aprotischen polaren Lösungsmittel;
   - das aprotische polare Lösungsmittel entfernt; und
   - ein Polyimid-Verbundmaterial bildet, in dem 0,01 bis 50 Gew.-Teile des mit Einlagerungen versehenen Tonminerais einheitlich in 50 bis 99,99 Gew.-Teilen des Polyimids dispergiert sind.

8. Verfahren zur Herstellung eines Polyimid-Verbundmaterials nach Anspruch 7, worin das protische polare Lösungsmittel wenigstens eine Verbindung umfasst, die gewählt ist aus der aus Wasser, Methanol, Ethanol, Propanol, Isopropanol, Ethylenglykol, 1,4-Butandiol und Glycerin bestehenden Gruppe.

9. Verfahren zur Herstellung eines Polyimid-Verbundmaterials nach Anspruch 7 oder 8, worin die Lösung eine Lösung von Polyamsäure ist.

10. Verfahren zur Herstellung eines Polyimid-Verbundmaterials nach einem der Ansprüche 7 bis 9, worin das aprotische polare Lösungsmittel wenigstens ein amidartiges Lösungsmittel umfasst, das gewählt ist, aus der aus N,N-Dimethylacetamid, N-Methylpyrrolidon, N,N-Dimethylformamid und 1,3-Dimethylimidazolidinon bestehenden Gruppe.

Revendications

1. Matériau composite de polyimide qui comprend entre 0,01 et 50 parties en masse d'un minéral argileux à insertion dispersé uniformément dans 50 à 99,99 parties en masse d'une résine contenant du polyimide, dans lequel on peut obtenir ledit minéral argileux à insertion en faisant réagir un minéral argileux en couches avec des composés de mono-onium organique ne possédant qu'un ion onium à une extrémité de leur chaîné principale et étant exempts de groupements du type amino, carboxyle, époxyde, hydroxyle, vinyle et d'autres groupements fonctionnels capables de réagir avec un polymère.

2. Matériau composite de polyimide selon la revendication 1, dans lequel l'ion mono-onium organique est au moins un élément choisi dans le groupe constitué de l'ion monoammonium, de l'ion monopyridinium, de l'ion monophosphonium et de l'ion monosulfonium.

3. Matériau composite de polyimide selon la revendication 1 ou la revendication 2, dans lequel l'ion mono-onium organique possède une chaîne principale qui est constituée de 6 à 20 atomes de carbone.

4. Matériau composit de polyimid selon l'une qu lconqu des r v ndications 1 à 3, dans l quel le minéral argil ux en couches est au moins un élément choisi dans le group constitué de minéraux argileux de type smectite comprenant la montmorillonite, la saponite, la béidellite, l'hectorite et la stévensite ; de la vermiculite ; de l'halloysite ; et du mica capable de gonfler.

5. Matériau composit de polyimide selon l'une quelconque des revendications 1 à 4, dans lequel le minéral argil ux n couches à insertion est dispersé, de sorte que les couches individuelles sont séparées les unes des autres au niveau moléculaire.

6. Matériau composite de polyimide selon l'une quelconque des revendications 1 à 5, lequel comprend de plus au moins un composant choisi dans le groupe constitué de résines autres que de polyimide, de pigments, de colorants, de fibres de verte, de fibres métalliques, de particules métalliques, de stabilisants à la chaleur, d'antioxydants, d'absorbants de la lumière ultraviolette, de stabilisants à la lumière, de lubrifiants, de plastifiants, d'agents antistatiques et d'agents ignifuges.

7. Procédé de production d'un matériau composite de polyimide, lequel comprend les étapes consistant à :

- insérer dans un minéral argileux en couches des composés de mono-onium organique ne possédant qu'un ion onium à une extrémité de leur chaîne principale et étant exempts de groupements du type amino, carboxyle, époxyde, hydroxyle, vinyle et d'autres groupements fonctionnels capables de réagir avec un polymère par un mélange dans un solvant protique polaire ;
- ajouter en mélangeant le minéral argileux à insertion, à partir duquel on élimine ledit solvant protique polaire, à une solution obtenue en dissolvant un monomère ou un prépolymère du polyimide dans un solvant aprotique polaire ;
- éliminer le solvant aprotique polaire ; et
- former un matériau composite de polyimide dans lequel de 0,01 à 50 parties en masse dudit minéral argileux à insertion est dispersé uniformément dans 50 à 99,99 parties en masse dudit polyimide.

8. Procédé de production d'un matériau composite de polyimide selon la revendication 7, dans lequel ledit solvant protique polaire comprend au moins un élément choisi dans le groupe constitué de l'eau, du méthanol, de l'éthanol, du propanol, de l'isopropanol, de l'éthylèneglycol, du 1,4-butanediol et du glycérol.

9. Procédé de production d'un matériau composite de polyimide selon la revendication 7 ou la revendication 8, dans lequel ladite solution est une solution de poly(acide amique).

10. Procédé de production d'un matériau composite de polyimide selon l'une quelconque des revendications 7 à 9, dans lequel ledit solvant aprotique polaire comprend au moins un solvant de type amide choisi dans le groupe constitué du N,N-diméthylacétamide, de la N-méthylpyrrolidone, du N,N-diméthylformamide et de la 1,3-diméthylimidazolidinone.